

29

# PATENT SPECIFICATION

(11) 1 232 257

DRAWINGS ATTACHED

1 232 257

- (21) Application No. 44780/68 (22) Filed 20 Sept. 1968  
(31) Convention Application No. P 16 43 666.1  
(32) Filed 23 Sept. 1967 in  
(33) Germany (DT)  
(45) Complete Specification published 19 May 1971  
(51) International Classification C 07 c 33/04  
(52) Index at Acceptance  
C2C 3A13A1A1 3A13A1K 3A13A3A1D 3A13A3B1  
3A13A3K



## (54) PRODUCTION OF PROPARGYL ALCOHOL

(71) We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESellschaft, a German Joint Stock Company, of Ludwigshafen/Rhein, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved process for the production of propargyl alcohol by reacting formaldehyde with acetylene.

It is known from British Patent Specification No. 508,062 that propargyl alcohol is obtained by reacting aqueous formaldehyde with acetylene in the presence of copper, silver, gold or mercury or a compound thereof. The yields of propargyl alcohol achieved in these methods are however less than 10% of the theoretical yields. According to other methods described in British Patent Specification Nos. 508,062 and 676,601 and in U.S. Patent Specification No. 3,087,970 better yields of propargyl alcohol are obtained by reacting aqueous formaldehyde with acetylene in the presence of solvents for acetylene and in the presence of copper acetylide. The methods have the disadvantage however that relatively large amounts of formaldehyde are not reacted and have to be separated from the propargyl alcohol at great expense. It is also known from the process described in U.K. Patent Specification No. 968,928 that the reaction of aqueous formaldehyde with acetylene in the presence of copper acetylide which has been activated with alkali metal or alkaline earth metal bromides or iodides, results in the formation of propargyl alcohol, the formaldehyde used being largely consumed. This method has the disadvantage that the alkali metal or alkaline earth metal halides used as activators are quickly washed out from the catalyst and therefore have to be constantly replaced. The solution of propargyl alcohol thus produced consequently contains halides which considerably disturb further processing par-

ticularly of the butynediol formed as a by-product, for example by hydrogenation.

We have now found that the production of propargyl alcohol by reaction of formaldehyde with acetylene, preferably in the presence of an organic solvent for acetylene, at elevated temperature and at superatmospheric pressure in the presence of copper acetylide supported on a carrier can be carried out more advantageously than hitherto when the reaction is carried out in a plurality of successive stages, a molar ratio of dissolved acetylene to propargyl alcohol of from 1.1:1 to 15:1 being maintained in the second and in the subsequent reaction stages, if any.

The new process has the advantage that good yields of propargyl alcohol can be obtained. Moreover the solution of propargyl alcohol prepared as a rule contains only very small amounts of formaldehyde so that the processing of the propargyl alcohol is greatly simplified. Moreover the reaction mixture does not as a rule contain any halides or other substances which might disturb further processing.

The formaldehyde is generally used in the form of a aqueous solution, advantageously diluted with an organic solvent for acetylene which is miscible with the aqueous formaldehyde. The concentration of formaldehyde in the solution is advantageously 1 to 25%, particularly 2 to 15%, by weight with reference to the whole of the mixture. It is also possible to use paraformaldehyde or polyoxymethylene in suspension or solution instead of the aqueous formaldehyde solution. The reaction is preferably carried out in the presence of a solvent for acetylene. Those solvents for acetylene are preferred which under the reaction conditions will absorb more than 2 cm<sup>3</sup> of gaseous acetylene per cm<sup>3</sup> of solvent. Examples of suitable solvents are cyclic ethers such as tetrahydrofuran, dimethyltetrahydrofuran, hexamethylene oxide or dioxane; lactones such as butyrolactone; disubstituted amides such as N-

[Price 25p]

methylpyrrolidone and dimethyl formamide; acetals such as formaldehyde dimethyl acetal; and alcohols such as methanol. Lactones having five to seven ring members are preferred as solvents.

5 The reaction is advantageously carried out at temperatures of 70° to 150°C, particularly of 80° to 130°C. The reaction takes place at superatmospheric pressure. It is advantageously to use pressures of up to 60 atmospheres partial pressure of acetylene. Higher pressures may be produced by forcing in an inert gas such as nitrogen. It is preferred to carry out the reaction at 15 pressures of up to 500 atmospheres and it is advantageous to ensure that a gas phase does not form in the reaction vessel. Copper acetylide on a carrier is used as the catalyst. Examples of suitable carriers are silica gel, 20 pumice or active carbon. The supported catalysts advantageously contain 8 to 25% of copper acetylide with reference to the sum of carrier and copper acetylide. Preferred catalysts contain not only copper 25 acetylide but also additives such as bismuth oxide in an amount of from 10 to 40% by weight with reference to the content of copper acetylide.

An essential feature of the invention is 30 carrying out the reaction in a plurality of successive stages; it is advantageous to use two to five, particularly three or four, successive reaction stages. The reaction in the individual stages is advantageously carried out in such a way that fresh acetylene is supplied to each reaction stage separately. It is 35 advantageous to introduce 0.5 to 150, particularly 1 to 60, moles of dissolved acetylene into each individual reaction stage for each mole of formaldehyde present.

Another essential feature of the invention is the use in the second stage and in the subsequent stages, if any, of an amount of feed acetylene such that a molar ratio of dissolved acetylene to propargyl alcohol present of 1.1:1 to 15:1, particularly 6:1 to 15:1, is maintained. It is advantageous to select the reaction conditions so that in the second stage and in the subsequent stages, if any, less than 50 4, preferably less than 2, moles of formaldehyde is present for each mole of propargyl alcohol.

The process according to the invention may be carried out for example by passing 55 the formaldehyde solution and the acetylene concurrently downwards over a fixed-bed catalyst.

A diagrammatic drawing of apparatus suitable for this method is shown in Figure 1. 60 Formaldehyde solution preheated to the reaction temperature and having the specified concentration and composition is metered by a feed pump 1 into the upper portion of a reaction tube 2 in which the said catalyst is arranged in a fixed bed. At the same time

acetylene is fed through a compressor 9 and gas preheater 10 into a stabilizing zone 11 filled with Raschig rings. Formaldehyde solution and acetylene are passed cocurrently over the fixed-bed catalyst and the reaction mixture is separated into a gaseous phase and a liquid phase in a high pressure separator 3 downstream of the same. The gaseous constituents are returned to the gas preheater 10 through a cooler 7 and a gas circulation pump 8. The liquid constituents are discharged from the high pressure separator 3 through a valve 4 and passed through a cooler 5 into a separator 6 whence the reaction solution is forced into the second stage. The following stages are constructed in the same way. Propargyl alcohol is isolated, for example by fractional distillation, from the reaction mixture obtained after from two to five reaction stages.

It is also possible to carry out the process in a liquid phase, i.e. without maintaining a gas phase in the reactor.

According to a preferred embodiment (shown diagrammatically in Figure 2) formaldehyde solution (with or without a suitable solvent) is metered through a pump 12 and acetylene through a pump 13 into a cooled saturator 14. Pump 15 withdraws from the saturator 14 such an amount of reaction solution that a constant level is maintained and meters it into the bottom of a reaction tube 16 which is filled with the catalyst described. Conditions are correlated so that no gas phase is present in the reaction tube 16. The said reaction temperature and pressure is maintained in the reaction tube 16. The reaction solution passes through a pressure maintaining valve 17 into a separator 18 in which the gaseous constituents are separated. The reaction solution is passed from the separator 18 into the following reaction stages which are constructed in the same way as the first reaction stage. Naturally in the following reaction stages the reaction solution discharged from the preceding stage is used instead of formaldehyde solution.

Propargyl alcohol prepared by the process according to this invention is a starting material for the production of pest control agents and of 2-aminopyrimidine which is used in the synthesis of pharmaceuticals (see Liebig's Annalen 596, Äthinylierung (Ethynylation), page 99).

The invention is illustrated by the following Examples in which parts are by weight unless otherwise stated. They bear the same relation to parts by volume as the kilogram to the liter.

#### EXAMPLE 1

800 parts by volume of a mixture containing 8% by weight of formaldehyde, 12% by weight of water and 80% by weight of butyrolactone is metered per hour into a 130

7.8% by weight of propargyl alcohol, 2.44% by weight of butynediol and 0.41% by weight of formaldehyde. The yield with reference to formaldehyde is 94% of the theory. Sufficient acetylene is introduced into the second reaction stage to maintain a molar ratio of dissolved acetylene to propargyl alcohol of from 1.1:1 to 15:1.

# WHAT WE CLAIM IS:—

1. A process for the production of propargyl alcohol by reaction of formaldehyde with acetylene at elevated temperature and at superatmospheric pressure in the presence of copper acetylide supported on a carrier wherein the reaction is carried out in a plurality of successive stages and a molar ratio of dissolved acetylene to propargyl alcohol of from 1.1:1 to 15:1 is maintained in the second reaction stage and in the following reaction stages, if any.
2. A process as claimed in claim 1 wherein a 1 to 25% by weight aqueous solution of formaldehyde is used.
3. A process as claimed in claim 1 or 2 wherein the reaction is carried out in the presence of a solvent for acetylene which under the reaction conditions absorbs more than 2 cm<sup>3</sup> of gaseous acetylene per cm<sup>3</sup> of solvent.
4. A process as claimed in any of claims 1 to 3 wherein a lactone having from five to seven ring members is used as a solvent.
5. A process as claimed in any of claims 1 to 4 carried out at a temperature of from 70° to 150°C.
6. A process as claimed in any of claims 1 to 5 wherein an acetylene partial pressure of up to 60 atmospheres is used.
7. A process as claimed in any of claims

1 to 6 wherein a total pressure of up to 500 atmospheres is used.

8. A process as claimed in any of claims 1 to 7 wherein the reaction is carried out in a reaction zone where there is no gas phase present.

9. A process as claimed in any of claims 1 to 8 wherein the supported catalyst contains from 8 to 25% by weight of copper acetylide with reference to the sum of carrier and copper acetylide.

10. A process as claimed in any of claims 1 to 9 wherein the supported catalyst contains copper acetylide and 10 to 40% by weight of bismuth oxide with reference to the content of copper acetylide.

11. A process as claimed in any of claims 1 to 10 wherein from two to five successive reaction stages are used.

12. A process as claimed in any of claims 1 to 11 wherein from 0.5 mole to 150 moles of dissolved acetylene is used per mole of formaldehyde present in every reaction stage.

13. A process as claimed in any of claims 1 to 12 wherein from 1 to 60 moles of dissolved acetylene is used in every reaction stage per mole of formaldehyde present.

14. A process as claimed in claim 1 carried out substantially as described in any of the foregoing Examples.

15. Propargyl alcohol when obtained by the process claimed in any of claims 1 to 14.

J. Y. & G. W. JOHNSON,  
Furnival House,  
14-18 High Holborn,  
London, W.C.1.  
Chartered Patent Agents,  
Agents for the Applicants.

vertical tube having a capacity of 3000 parts by volume (cf. Figure 1) which contains 2500 parts by volume of a catalyst consisting of 15% by weight of copper acetylide and 4% by weight of bismuth oxide on silica fragments having a diameter of 3 to 8 mm. At the same time acetylene at superatmospheric pressure is passed into the top of the reaction tube so that a pressure of 12.5 atmospheres gauge and a temperature of 95°C are maintained in the reaction tube. The reaction solution is freed from gaseous constituents in a separator 3 (C8 Figure 1). It contains 2.29% by weight of formaldehyde and 4.1% by weight of propargyl alcohol. This solution is reacted in a second reaction tube under the same reaction conditions. After the second reaction stage, the reaction solution contains 0.85% by weight of formaldehyde and 4.8% by weight of propargyl alcohol. The reaction product from the second reaction tube is reacted with acetylene in the third reaction tube under the same conditions as in the preceding stages. From the third reaction tube a product is obtained containing 5.14% by weight of propargyl alcohol, 7% by weight of butynediol and 0.30% by weight of formaldehyde. Sufficient acetylene is introduced into the second and third reaction tubes to maintain the molar ratio of dissolved acetylene to propargyl alcohol within the range 1.1:1 to 15:1.

#### EXAMPLE 2

The procedure of Example 1 is followed but the feed is a solution consisting of 6% by weight of formaldehyde, 9% by weight of water and 85% by weight of butyrolactone and the reaction is carried out in only two successive reaction tubes. From the first reaction tube a solution is obtained which contains 3.85% by weight of propargyl alcohol and 1.19% by weight of formaldehyde. From the second reaction tube a solution is obtained which contains 4.31% by weight of propargyl alcohol, 4.7% by weight of butynediol and 0.29% by weight of formaldehyde. Sufficient acetylene is introduced into the second reaction tube to maintain a molar ratio of dissolved acetylene to propargyl alcohol of from 1.1:1 to 15:1.

#### EXAMPLE 3

The procedure described in Example 1 is followed but the feed used is 400 parts by volume of a solution consisting of 10% by weight of formaldehyde, 40% by weight of water and 50% by weight of methanol. The reaction mixture is passed through three successive reaction tubes. After the first reaction tube the solution contains 4.17% by weight of propargyl alcohol and 3.27% by weight of formaldehyde and after the second reaction tube 4.86% by weight of propargyl alcohol and 1.32% by weight of formaldehyde. The solution discharged from the third reaction tube contains 5.1% by weight of

propargyl alcohol and 0.36% by weight of formaldehyde. Sufficient acetylene is introduced into the second and third reaction tubes to maintain a molar ratio of dissolved acetylene to propargyl alcohol of from 1.1:1 to 15:1.

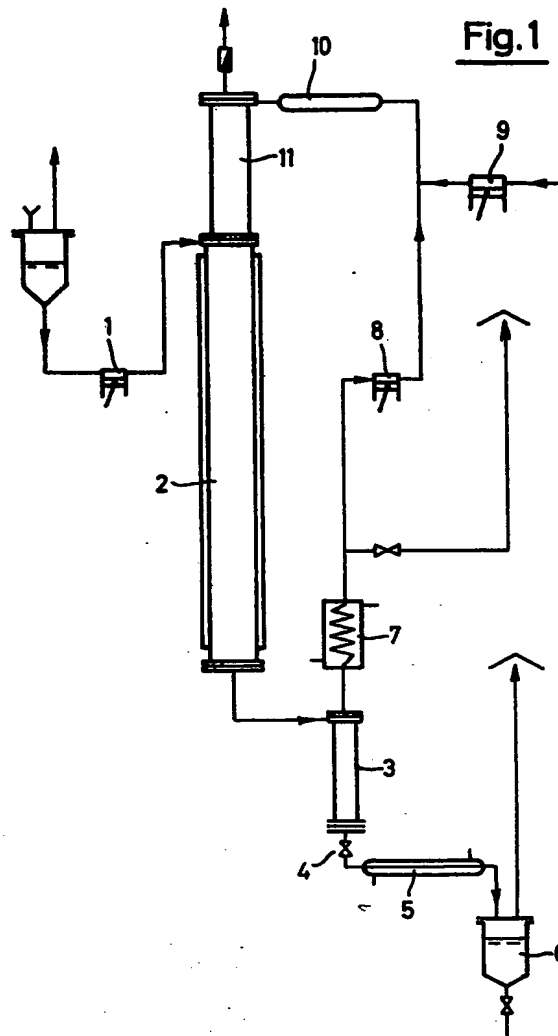
#### EXAMPLE 4

500 parts by volume of a 3.7% by weight aqueous formaldehyde solution per hour and such an amount of acetylene is passed into a cooled mixing vessel having a capacity of 2400 parts by volume (cf. Figure 2) that a pressure of 25 atmospheres is maintained. At the same time such an amount of reaction solution is withdrawn through a pump from the mixing vessel that it is constantly three-quarters full. The reaction solution is metered into the bottom of a vertical reaction tube having a capacity of 1000 parts by volume which is charged with a catalyst consisting of 12% of copper acetylide and 4% by weight of bismuth oxide on silica fragments and which is kept at an internal temperature of 95°C. No gas phase is allowed to form in the reaction tube. The reaction solution is passed from the top of the reaction tube through a constant-pressure valve adjusted to 200 atmospheres into a gas separator and freed from gaseous constituents. The reaction solution obtained contains 0.95% by weight of formaldehyde and 2.7% by weight of propargyl alcohol. It is reacted with fresh acetylene in a second reaction stage of the same type under the same reaction conditions. The reaction solution contains 3.1% by weight of propargyl alcohol, 2.6% of butynediol and 0.24% by weight of unreacted formaldehyde after the second stage. Sufficient acetylene is introduced into the second reaction stage to maintain a molar ratio of dissolved acetylene to propargyl alcohol of from 1.1:1 to 15:1.

COMPARISON EXAMPLE: The procedure of Example 4 is followed but only the first stage of the reaction is used, the residence time being doubled. The reaction product contains 2.68% by weight of propargyl alcohol, 2.6% by weight of butynediol and 0.43% by weight of formaldehyde.

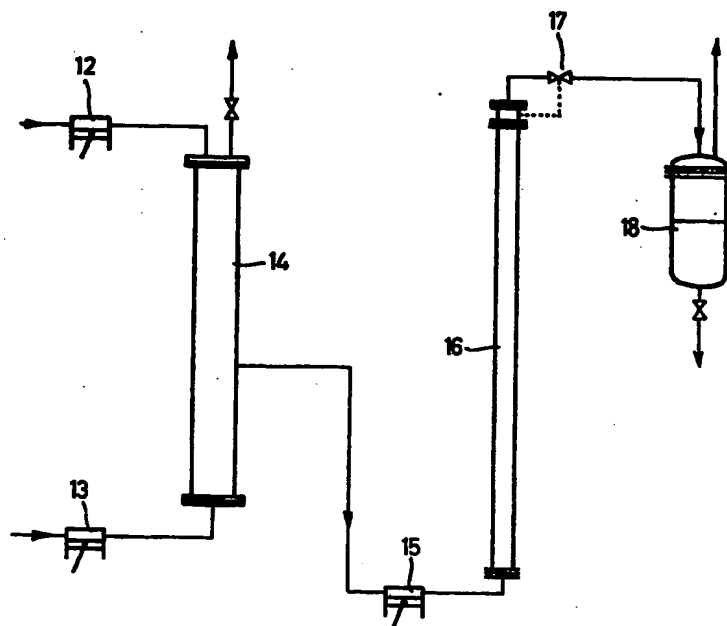
#### EXAMPLE 5

The procedure described in Example 4 is followed but 400 parts by volume per hour of a solution consisting of 6.3% by weight of formaldehyde, 23.7% by weight of water and 70% by weight of butyrolactone is metered in. An acetylene pressure of 20 atmospheres is maintained in the mixing vessel 14, each liter of formaldehyde solution absorbing 250 liters of acetylene. From the first reaction tube, a solution is obtained which contains 6.38% by weight of propargyl alcohol and 1.32% by weight of formaldehyde. After the solution thus obtained has passed under identical conditions through an identical apparatus (Figure 2), the solution contains



THIS PAGE BLANK (USPTO)

**Fig. 2**



THIS PAGE BLANK (USPTO)